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N668 N671 N771  
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(54) Impact resistant laminate

(57) A translucent impact resistant laminate comprises at least three translucent panes (4), (6), (8) which are bonded together by at least two translucent interlayers (10), (12) formed from a thermosetting plastics resin, each pair of adjacent panes being bonded together by a respective one of the translucent interlayers. The resin may be epoxy resin. The interlayers may incorporate an organic boron-containing glass forming component which is not a curing agent for the resin.

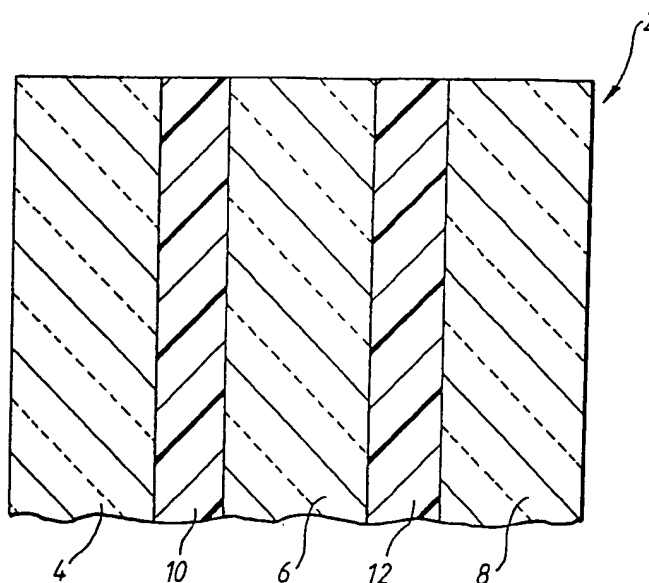


Fig.1

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

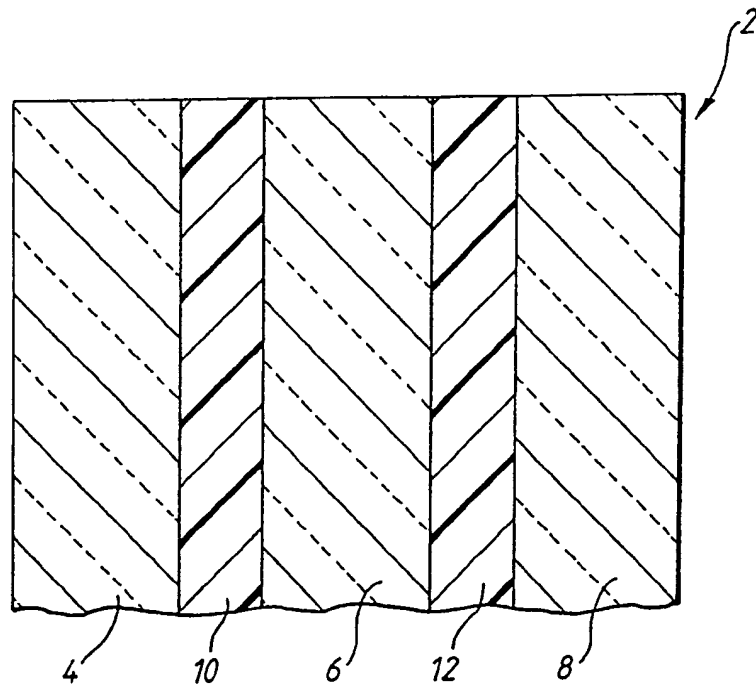


Fig.1

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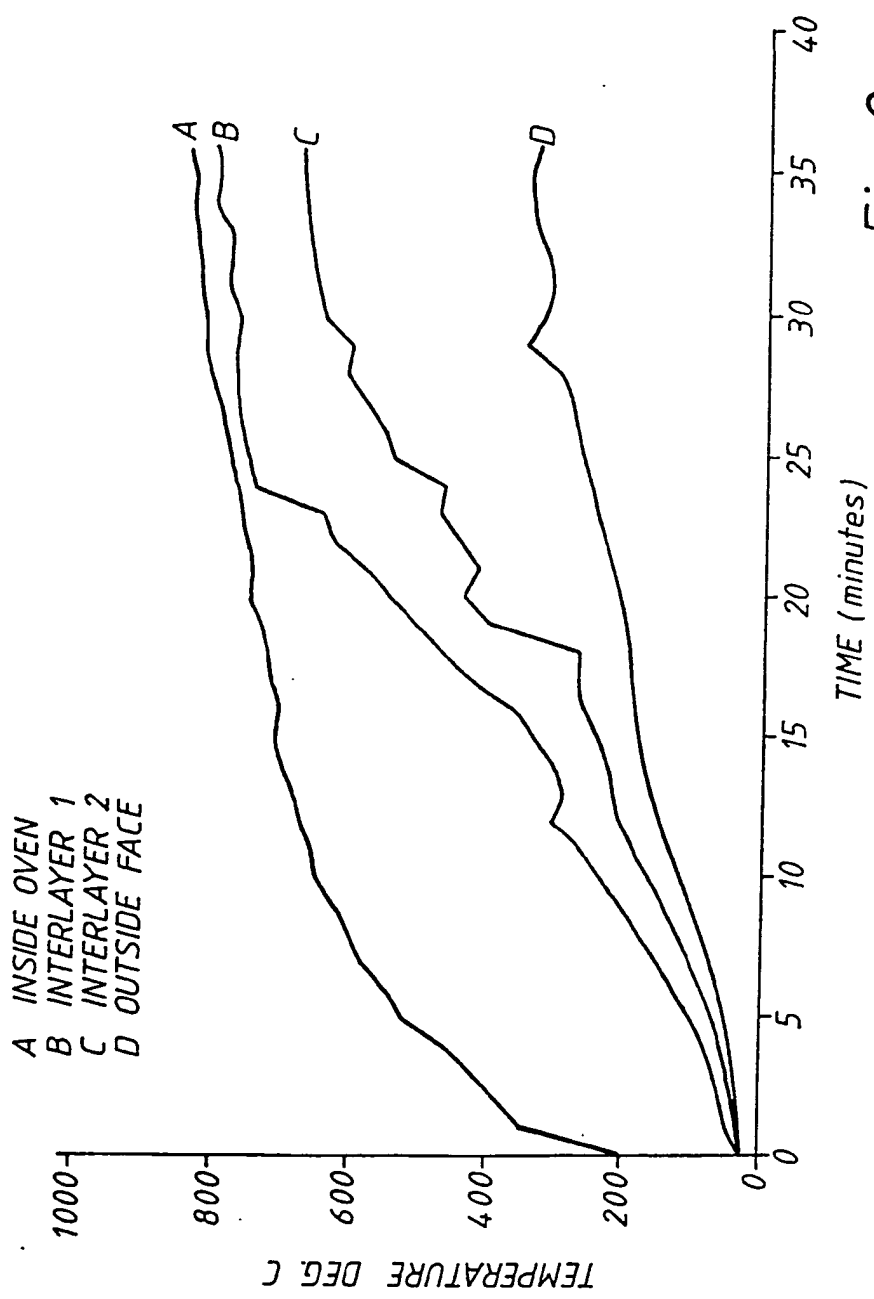


Fig. 2

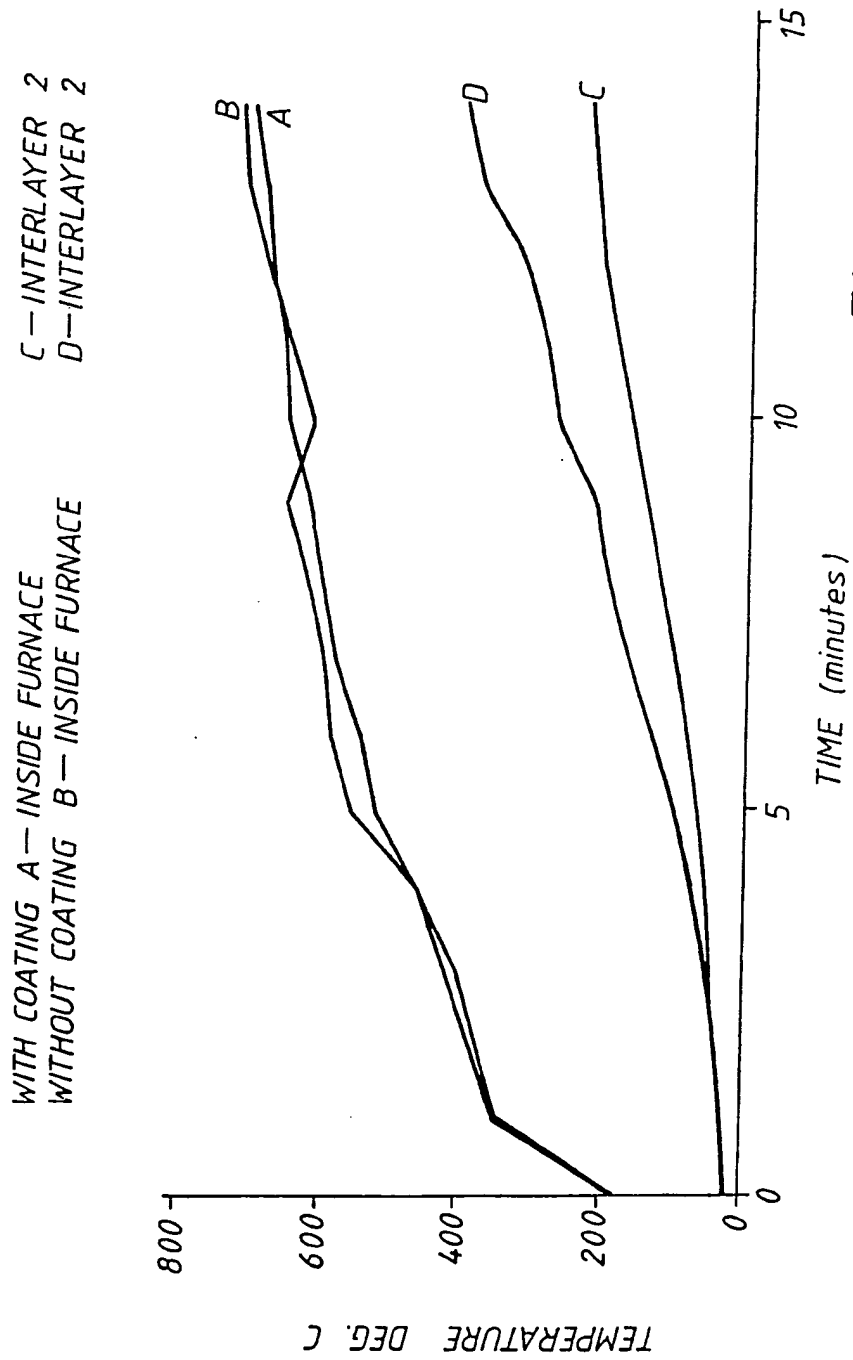


Fig. 3.

IMPACT RESISTANT LAMINATES AND  
MANUFACTURE THEREOF

The present invention relates to a translucent laminate having impact resistance, a method of producing such a laminate, a method of improving the impact resistance of such a laminate and the use of a laminate as an impact resistant glazing pane. The present invention has particular application in the manufacture of impact resistant laminates which also have fire resistance.

It is known to use thermosetting resins for the manufacture of interlayers in translucent impact resistant laminates. For example, epoxy resin reaction mixtures and reaction products are used as thermosetting resins for manufacture of aircraft windows. GB-B-1058076 discloses a reaction mixture comprising a transparent blend obtained from an epoxy resin, trimethoxyboroxine and a phenyl substituted alkyl alcohol, especially benzyl alcohol. The trimethoxyboroxine is used as a curing agent for the epoxy resin which may be of the bisphenol-A type, the bisphenol-F type or the novalac type. The epoxy resin has incorporated therein organic phosphorous compounds to improve its fire resistance. The interlayer formed from the epoxy resin may be disposed between transparent plies composed of acrylics, polycarbonates and silicate glass.

Thermosetting resins such as epoxy resins are used to form interlayers in fire resistant translucent laminates since the cured epoxy resin reaction products tend to form a char on heating rather than to melt, thus retaining the structural integrity of the laminate when it is subjected to a fire. Epoxy resins are well known as structural adhesives because of such properties as good wetting and the formation of strong, polar, high-energy bonds to a variety of substrates; low cure shrinkage without the evolution of low molecular weight substances; good mechanical properties, and

environmental stability. In accordance with the teaching of the prior art, it is believed that structural thermosetting adhesives with good elevated temperature capability require high glass transition temperatures ( $T_g$ ) in order for the adhesive strength to be maintained at high temperatures. Thus it is believed in the art that a high  $T_g$  is required to enable the epoxy resin to be used in a fire resistant laminate. However, cured epoxy resins with relatively high  $T_g$  have the fundamental drawback in that they are brittle so that on impact the brittleness of the epoxy resin can cause catastrophic failure of the adhesive layer. Thus, it is known in the art that epoxy resin interlayers have been utilised in glass and plastics laminates to provide good fire resistant properties but that the laminates may not have good impact resistance. It is also known in the art to employ thermosetting resin interlayers in translucent laminates formed from materials other than epoxy resins. There is a general need to improve the impact resistance of such resin interlayers as well.

The present invention aims to provide translucent laminates having good impact resistance, and optionally good fire resistance, by the use of thermosetting resin interlayers in combination with a specifically designed laminate structure.

The present invention accordingly provides a translucent laminate having impact resistance, the laminate comprising at least three translucent panes which are bonded together by at least two translucent interlayers formed from a thermosetting plastics resin, each pair of adjacent panes being bonded together by a respective one of the translucent interlayers.

The present invention also provides a method of producing a translucent laminate having impact resistance, the method comprising the steps of providing at least three

translucent panes and forming from a thermosetting plastics resin at least two translucent interlayers between the at least three translucent panes whereby a respective one of the translucent interlayers is disposed between each adjacent pair of translucent panes.

The present invention further provides a method of improving the impact resistance of an impact resistant translucent laminate comprising a plurality of translucent panes and at least one interlayer ply, the or each interlayer ply being formed from thermosetting plastics resin and disposed between an adjacent pair of translucent panes, the total thickness of each of the laminate, the translucent panes and the at least one interlayer ply being predetermined, the method comprising increasing the number of translucent panes and the number of interlayer plies whilst substantially maintaining each of the said predetermined total thicknesses.

The present invention still further provides use as an impact resistant glazing pane of a laminate having a plurality of glass plies with at least one thermoset interlayer between adjacent glass plies, characterised in that to improve the impact resistance the total thickness of glass is divided between at least three separate glass plies and the total thickness of thermosetting interlayer is divided between at least two separate interlayer plies.

Embodiments of the present invention will now be described by way of example only, with reference to the accompanying drawings, in which:-

FIG. 1 is a schematic section through a glass laminate in accordance with the present invention; and

FIGS. 2 and 3 are graphs showing the results of temperature measurement tests carried out on fire resistant laminates in accordance with the present invention.

In accordance with one aspect of the present invention, the present inventors have discovered surprisingly that for a translucent impact resistant laminate of predetermined total thickness and for a predetermined total thickness of each material in the laminate, the division of those material thicknesses into an increased number of plies causes a substantial improvement in impact resistance of the laminate.

The preferred thickness of a laminate in accordance with the present invention is up to about 10 mm. For architectural glazing purposes, a standard frame rebate for safety glazing having fire and/or impact resistance is 8 mm. Thus there is a need for a fire and/or impact resistant laminate having a maximum thickness of 8 mm which can fit into such a rebate. The present inventors have aimed to provide a laminate providing both fire and impact resistance which has a predetermined thickness of 8 mm so that it can fit into such a rebate but which has improved impact resistance whilst maintaining good fire resistance. The present inventors initially tested 3 ply 8 mm thick laminates having two plies of 3 mm thick float glass separated by a single ply of 2 mm thick interlayer of cured epoxy resin. Thus the total structural ply thickness was 6 mm and the total interlayer thickness was 2 mm. The inventors discovered surprisingly that by modifying the laminate so as to provide a 5 ply laminate of total thickness 8 mm, and having three structural plies of float glass each being 2 mm thick and two interlayer plies of cured epoxy resin each 1 mm thick, a substantial improvement in impact resistance of the total laminate resulted. The invention is also applicable to other thicknesses both of the entire laminate and of the component plies of the laminate. For a laminate having five plies and a total thickness of around 10 mm, this may be composed of three 2.8 mm thick float glass plies and two 1 mm thick interlayers of cured epoxy resin.



The present inventors have also discovered that by increasing the number of plies of a laminate, the glass transition temperature  $T_g$  of the interlayer material can be increased relative to that of the interlayer employed in the laminate having a reduced number of plies whilst giving improved impact resistance performance. The glass transition temperature  $T_g$  of the polymeric interlayer material is defined as the temperature at which amorphous domains of the polymer take on the characteristic properties of the glassy state i.e brittleness, stiffness and rigidity. The  $T_g$  is measured by dynamic mechanical thermal analysis (DMTA). For example, the present inventors have discovered that for a 3 ply laminate of the type described above, the  $T_g$  of the epoxy resin interlayer can be a maximum of about  $41^{\circ}\text{C}$  in order to pass Class C of the impact test under the British Standard test BS 6206 for impact resistant laminates. In contrast, a corresponding 5 ply laminate of the type described above can utilise interlayers having much higher values of  $T_g$ , for example up to about  $63^{\circ}\text{C}$ , whilst still enabling both Class C, and the higher Class B, of the impact test under BS 6206 to be passed.

Thus the present invention enables interlayers of thermosetting resin having higher values of  $T_g$  than in the prior art to be employed in impact resistant laminates whilst still giving good impact performance. This not only broadens the range of interlayer compositions which can be employed in impact resistant laminates for given impact resistance requirements, but also, when the laminate is to be used as a fire resistant laminate, enables thermosetting interlayer materials of higher  $T_g$  than in the prior art to be employed which in turn can improve the fire resistance of the laminate.

Furthermore, the fire resistance of the laminates of the present invention is improved by having lower interlayer thicknesses and an increased number of structural plies. The reduction in the interlayer thickness reduces the possibility of cohesive failure of the interlayer when the

interlayer is heated by a fire. Fire resistance of a laminate requires a minimum value of  $T_g$  otherwise when the interlayer is heated it rapidly softens so that it cannot hold the weight of the pane which faces the fire and the integrity of the laminate fails by cohesive failure of the interlayer. The use of a low thickness high  $T_g$  interlayer compared to the prior art reduces the possibility of such a softening and cohesive failure. An increase in the number of structural plies also reduces the possibility of a through failure which results, when, as a result of being subjected to a fire, the structural panes of the laminate crack with substantial coincidence of cracks in adjacent panes permitting smoke and flames to pass therethrough. An increase in the number of structural plies reduces the possibility of such crack coincidence in adjacent panes and therefore reduces the possibility of smoke and flame penetration through the laminate.

The improvement in impact performance which is achieved in accordance with the invention by utilising a larger number of thinner interlayers of thermosetting resin is based on the surprising discovery that for thermosetting resins, particularly epoxy resins, a decrease in thickness of the resin interlayer actually decreases the brittleness of the layer. Prior to the present invention, it was believed that because thermosetting resins such as epoxy resins have residual stresses therein when formed into interlayers, when a relatively thick e.g. 2 mm thermosetting resin interlayer which is relatively brittle was reduced in thickness then the brittleness would be increased as a result of these residual stresses. Surprisingly, the inventors of the present invention have discovered that such a decrease in thickness does not actually increase the brittleness of the thermosetting resin interlayer. The thermosetting resin interlayer has been found to have a greater elongation at break when the thickness of the interlayer is reduced. In addition, in macro testing, in

which the impact strength of a resultant laminate is tested, for example in accordance with the test of BS 6206, the provision of an increased number of thinner interlayers increases the impact strength of the laminate as a whole, despite the fact that the laminate has the same total thickness and the total thickness of the constituents of the laminate, i.e. the structural plies and the interlayer plies, remain the same. It is believed, without being bound by theory, that an increase in the number of interlayers in accordance with the present invention whilst retaining the total thickness of the interlayers the same, results in a greater impact resistance of the laminate as a whole because each interlayer, being thinner, is more capable of slight elastic deformation when it is impacted as compared to a thicker interlayer. Furthermore, it is believed that the increase in impact resistance results from interfacial effects between the thermosetting resin and the structural plies which tend to reduce the brittleness of the thermosetting resin interlayers.

The fire resistance of the laminates in accordance with the invention is dependent upon the size of the total glazing area of the laminate. It is very important in the manufacture of fire and impact resistant laminates that it is possible to obtain fire and impact performance for large glazing areas. As the glazing area is increased, the size of the individual structural plies and of the interlayers are increased. This tends to reduce the fire performance, because of the increased weight of the outer glass ply which is subjected to a fire which is required to be supported by the adjacent interlayer which itself is being softened as a result of being subjected to heat.

The present inventors have found that for a 3 ply laminate having a single interlayer of thermosetting epoxy resin and which had sufficient impact resistance to at least class C of BS 6206, the required minimum fire resistance

criterion can be met only up to a maximum size of about 1 m<sup>2</sup> of the laminate. This is because the larger sizes could not meet the fire test specified.

The minimum fire resistance was specified as being the ability for a sample of the laminate to survive for a period of 30 minutes the fire test specified in British Standard BS 476, Parts 20 and 22. In that test, the sample laminate is placed in a frame in a wall of a furnace and the inner face of the laminate is heated by the furnace. The sample passed the test if the stability and integrity of the unexposed face, determined in accordance with BS 476, was maintained for the 30 minute test period. For commercial acceptance, as a fire and impact resistant laminate the laminate needs to pass the fire test at sizes up to about 1.6 m<sup>2</sup>, typically 2 m x 0.8 m.

The minimum impact resistance was the requirement to meet Class C of BS 6206.

In contrast, a 5 ply laminate produced in accordance with the present invention, including two interlayers of thermosetting resin, could pass both the above-specified fire test up to 2 x 1.2 m and the above-specified impact test.

The present invention is illustrated but not limited by the following Examples.

In the following Examples, which utilise a 5 ply laminate, and the following Comparative Examples which employ a 3 ply laminate, the laminates were fabricated as described hereinbelow and were then subjected to impact tests.

EXAMPLES 1 to 21

A number of 5 ply laminates were constructed in accordance with the invention using various interlayer compositions and various process parameters for the manufacture of the interlayers.

Table 1 shows the compositions of the thermosetting epoxy resin mixtures of Examples 1 to 21 which were used to form the laminate interlayers in accordance with the present invention.

The bisphenol F epoxy resin constituted the thermosetting resin for forming the epoxy resin interlayers in accordance with the present invention. As an alternative to bisphenol F epoxy resin, epoxy resins of the bisphenol-A type or the novalac type may be employed in accordance with the present invention. The epoxy resins should be translucent when a translucent body is required for example as the interlayer of a fire resistant laminate to be used as a window. Blends or mixtures of these epoxy resins may be used in accordance with the invention.

DER 736 and DER 732 are particular types of reactive diluents which have reactive groups which react with the epoxy resin material thereby to form a chemically modified (i.e. plasticised) epoxy resin molecular structure in the interlayer. The reactive diluents may contain epoxide reactive groups or reactive groups other than epoxides. The inventors have found in particular that in order to preserve the physical properties of epoxy resin interlayers at elevated temperatures, di- or polyepoxy reactive diluents are preferably employed. The reactive diluents act to change the cross link density of the epoxy system and thus the physical and chemical properties of the epoxy resin. DER 732 is a long chain diepoxide and DER 736 is a shorter chain variant thereof. DER 736 and 732 are flexible

polyglycol diepoxides (otherwise called polyoxyalkylene diglycidyl ethers) which are available in commerce from Dow Chemicals, UK. DER 736 has an epoxide equivalent weight of 175 to 205 mmol/kg, a viscosity of 30-60 centipoise at 25°C, a Colour Gardner (max) of 1, a density of 1.14 g/cm<sup>3</sup> and a flashpoint of 170°C. DER 732 has a epoxide equivalent of 305 to 335 mmol/kg, and a viscosity of 55 to 100 centipoise at 25°C, a Colour Gardner (max) of 1, a density of 1.06 g/cm<sup>3</sup> and a flashpoint of 205°C. DER 736 and DER 732 are flexible polyglycol diepoxides of exceptionally low viscosity and light colour so that when they are incorporated at low concentrations into an epoxy resin mixture, the mixture and the cured reaction product thereof are translucent. The use of reactive diluents to plasticise epoxy resins is disclosed in our co-pending British Patent Application No. 9203407.3.

Trimethoxyboroxine (TMB) is present as a curing agent for the epoxy resin. Trimethoxyboroxine acts as a Lewis acid capable of reacting with the epoxide groups in the epoxy resin. It is known for use in curing epoxy resins.

TCEP and Amgard V<sub>6</sub> are phosphates which are incorporated into the epoxy resins as fire retardent components. TCEP is tris-(2-chloroethyl) phosphate and Amgard V<sub>6</sub> is a chlorinated diphosphate ester available from Albright and Wilson Ltd of Warley, West Midlands, England. These flame retardents are known for use in epoxy resin mixtures for the manufacture of interlayers for laminates. The phosphates can also act as non-reactive diluents for the epoxy resins. Such diluents can lower the viscosity of the resin thereby facilitating the use of the resin during the formation of a cast-in-place interlayer.

Borester 7 and Borester 33 ("Borester" in a Registered Trade Mark) are added to the epoxy resin composition so as to increase the fire resistance of the composition.

Borester 7 is tri-(2-methyl-2,4-pentanediol) biborate a colourless liquid containing 5.9% by weight of boron and Borester 33 is hexylene glycol boric anhydride, a colourless to pale yellow liquid containing 7.5% by weight of boron. Both Borester 7 and Borester 33 are available in Commerce from US Borax, Inc. of Anaheim, California, USA. These organic boron compounds do not act as a curing agent for the epoxy resin. They are intended to provide boron (in the form of borate) into the interlayer so that when the interlayer is subjected to a fire, borate glass is formed in the interlayer which imparts fire resistance to the interlayer. Other boron-containing additives may be employed instead of Borester 7 and Borester 33. The use of boron additives to epoxy resins which do not act as curing agents for the epoxy resins so as to impact fire resistance to the cured resin is disclosed in our co-pending European Patent Application No. 92301317.1.

The additive Silane A-187, chemically known as glycidoxy propyl trimethoxysilane, is a trade name for the compound sold by Union Carbide Corporation although the compound is sold by other chemical companies. This compound acts as an interfacial coupling agent so as to promote adhesion between the epoxy resin and the structural panes of the laminate.

Benzyl alcohol is added as a moderator to control the rate of curing of the epoxy resin.

In Examples 1 to 21 the specified quantity of epoxy resin was placed in a reaction flask and the remaining components, apart from the trimethoxyboroxine curing agent, were added in the specified quantities. The mixture in the flask was warmed at between 20 and 25°C while stirring and degassing using a standard one stage vacuum pump to remove any entrapped air and volatiles.

Degassing was continued and 8.4 parts of trimethoxyboroxine was added as a curing agent to the mixture with stirring. Degassing was recommenced and, after 15 minutes stirring, was stopped. Degassing was continued for a further 15 minutes without stirring.

A laminate cell was made up which comprised two similar panes of 2 mm soda lime silicate float glass assembled in opposed facing relationship, with the adjacent panes being separated 0.8 mm apart by a polyurethane tape (made by 3M under product number 4032, "3M" being a registered trade mark). A similar tape was also used which was 1 mm thick and is sold by 3M under product number 4910F. The tape was disposed between the panes and extended around the peripheral margins of the pane. The tape is self-adhesive on both sides and originally was coated with removable release liners which cover the self-adhesive surfaces. The release liner on one self-adhesive surface along one edge of the cell structure was left on the tape. This was to allow the laminate cell to be opened. The reaction mixture described above was poured into the vertically held laminate cell to fill the cell completely and it was subsequently turned horizontal. The third sheet of glass was then assembled to the laminate and the above process was repeated.

In an alternative laminating method, samples were also made up as described in accordance with the laminating methods disclosed and claimed in EP-A-0490580 published 17th June 1992. In this alternative method, the first interlayer was left to gell for approximately 16 hours before the second interlayer was pumped into the laminate cell. It was found that this method gave a more even interlayer thickness than the first method disclosed above.

The interlayers in the laminates were then cured by first being gelled at room temperature (about 20°C) for a particular number of days, the gelling period being



indicated in Table 1 and then curing was then completed by the cells being placed horizontal in an oven for three hours at 120°C. The use of gelling to cure epoxy resins is disclosed in our co-pending British Patent Application No. 9203416.4. The resultant laminate, comprising three panes of clear float glass bonded together by two interlayers derived from the epoxy resin based reaction mixture was substantially transparent. The resultant laminate 2 is illustrated in Figure 1. It will be seen that three panes of float glass 4,6,8, each 2 mm thick, are bonded together to form a 5 ply laminate 2 by the two epoxy interlayers 10,12, each being 1 mm thick. The total laminate thickness is 8 mm.

The glass transition temperature Tg was measured for each of the interlayer materials thus formed and the values of Tg are specified in Table 1.

Referring to Table 2, the laminates formed in accordance with the Examples 1 to 21 were subjected to impact tests equivalent to those specified in BS 6206. BS 6206 requires at least four samples to be tested to obtain a certified pass of the standard, but in the Examples herein generally two samples of each interlayer formulation were tested. In Table 2, the column marked Impact Test Result indicates either the highest Class, either B or C, which the tested laminates would have met in accordance with the BS 6206 test or alternatively indicates the highest Class which would have been failed by the respective laminate. The Tg values of the laminates tested are indicated in ascending order.

In the impact test under BS 6206, the laminates tested were 1.930 x 0.865 m in dimension. It will be seen that, despite some variations in the test results, particularly with reference to Example 5 which failed to meet the criteria of Class C of the impact test and can be regarded

as an anomalous result, there is a good expectation of the laminate passing Class B of the impact test over a wide range of glass transition temperatures ranging from 38 to 63°C. These test results show that for a 5 ply laminate made in accordance with the invention, despite having thermosetting resin interlayers having high values of Tg up to about 63°C, very good impact performance is obtained. This impact performance results in the laminates being suitable for use as architectural fire and impact resistant laminates. The high glass transition temperature Tg values in Table 2 means that the fire performance of the laminate is improved as compared with laminates incorporating interlayers having lower levels of Tg. This is because a high Tg interlayer reaches a softening point later during the fire test than an interlayer of lower Tg. When lower Tg interlayers are employed, early softening of the interlayer during the fire test leads to a weakening of the overall structure and failure in the fire test as a result of the interlayer being unable to support the glass pane nearest the fire. The higher Tg materials soften later on during the fire test and this tends to retain the integrity of the laminate during the fire test and lead to improved fire performance.

#### COMPARATIVE EXAMPLES 1 to 12

Table 3 shows, in a manner similar to that of Table 1, the compositions of the interlayers of Comparative Examples 1 to 12 in which 3 ply, rather than 5 ply, laminates were produced and impact tested. Table 3 also shows the gelling time and the resultant Tg values of the interlayers. Laminates incorporating the interlayers were made broadly by the method described above with reference to Examples 1 to 21. However, in Comparative Examples 1 to 12, the laminates are 3 ply laminates rather than 5 ply laminates and thus have a single interlayer of thermosetting material disposed between two structural panes. In the Comparative Examples,

the two structural panes are each composed of 3 mm thick soda lime silicate float glass and the single interlayer is 2 mm thick, a correspondingly thick adhesive butyl tape having being employed in the manufacturing process. In each of the Comparative Examples, the total thickness of the laminate was 8 mm. For Comparative Examples 1 to 12, the total glass thickness and the total interlayer thickness in the 3 ply laminates are the same as those thicknesses of the 5 ply laminates of Examples 1 to 21.

The laminates of Comparative Examples 1 to 12 were subjected to the same impact tests as those to which the laminates of Examples 1 to 21 were subjected and the results are shown in Table 4.

It will clearly be seen that with the 3 ply laminates of the Comparative Examples, the laminates had considerably poorer impact resistance than the 5 ply laminates of Examples 1 to 21. This is despite the fact that the total laminate thickness is the same at 8 mm and the interlayer compositions, though varying in both the Examples and Comparative Examples, are substantially similar. It will also be noted that the impact resistance is strongly related to the corresponding value of the glass transition temperature  $T_g$  of the interlayer. It will be noted that Class C of the British Standard 6206 impact test was generally passed up to a  $T_g$  value of around  $41^{\circ}\text{C}$  but that at  $T_g$  values above that threshold, the laminates tended to fail Class C of BS 6206. When the results of Table 4 are compared to those of Table 2, it will be seen that for a wide variety of interlayer compositions including epoxy resin as a thermosetting resin, for a given thickness (i.e. 8 mm of laminate), a 5 ply laminate had considerably improved impact resistance compared to a 3 ply laminate, with each of those laminates having the same total thickness of structural plies and interlayer plies respectively. In addition, it will readily be seen that the use of a laminate

having a plurality of interlayer plies enables interlayer materials having much higher Tg values to be employed as compared to a 3 ply laminate having a single interlayer ply. This enables the high Tg interlayers to be employed to give good fire resistance whilst still retaining good impact resistance.

Furthermore, a significant advantage for fire resistance in employing a 5 ply structure as opposed to a 3 ply structure is that there is less probability of the phenomenon of through flaming and eventual failure of the laminate due to the increase in the number of plies.

By increasing the number of interlayers for a given total thickness of interlayer material in the laminate, this increases the impact resistance of the laminate. The interlayer should be even in thickness and not vary substantially in thickness over its area. Preferably, the minimum thickness of the interlayer is about 0.6 mm.

As has been shown in the results of the Examples and the Comparative Examples, for a 3 ply laminate having a single interlayer, in order to provide both fire and impact resistance the Tg of the interlayer should range from about 29°C to about 40°C. If the Tg is lower than about 29°C then the fire performance is poor because the interlayer softens so early during the fire test that it is unable to support the glass ply which faces the fire. If the Tg is raised above about 40°C, then the interlayer does not provide the necessary impact performance due to the brittle nature of the interlayer. With a multiple interlayer laminate fabricated in accordance with the present invention, the Tg of the interlayer material can range from about 29°C to about 63°C. Typical commercial laminates made in accordance with the present invention for fire and safety use having sizes greater than 1 m<sup>2</sup> would have a 5 ply laminate structure with the interlayer material

having a  $T_g$  of  $>60^{\circ}\text{C}$ . Thus the present invention can provide a high impact resistant fire resistant laminate which can satisfy stringent fire resistance tests and also can meet impact tests up to Class B of BS 6206. The laminate can be only 8 mm thick so as to be able to fit into a standard glazing rebate. The laminate also has the advantage that it is symmetric about its central plane. This means that in order to test the laminate for fire and impact resistance it is only necessary to test one side of the laminate since the properties of the laminate when tested on the other side would be the same. Furthermore, an advantage is that equal fire and safety resistance is provided on both sides of the laminate so that not only does the laminate provide the required fire and safety resistance on both sides thereof but equally it is irrelevant which way round the laminate is glazed into the rebate.

It is believed that the only commercially available fire and impact resistant laminate which meets the fire and glazing requirements which are achieved by the present invention and which is suitable for use in architectural glazing applications is a laminate called Pyrodur which is sold by an associate company of the applicant, namely Flachglas Aktiengesellschaft of Germany. This product is laminated with polyvinyl butyral which is a thermoplastic material. The Pyrodur laminate has a two glass panes and a layer of inorganic intumescent material. The product is 11 mm thick and so cannot fit into a standard rebate. In addition, the product is assymmetric and so it must be tested on both sides and glazed the right way round. The Pyrodur product meets Class B of the BS 6206 impact test and provides fire resistance similar to that attainable by the laminates of the present invention.

In accordance of a second aspect of the present invention, the fire resistant laminate, preferably consisting of a 5 ply laminate disclosed hereinabove, having

at least one thermosetting resin interlayer, preferably of epoxy resin, the interlayer including organic glass forming components, preferably borate-containing components, is provided with an infra-red reflecting fluorine-doped tin oxide coating on one or both of the exposed glass faces of the laminate. The use of such a coating is disclosed in the applicant's earlier EP-A-0389291 and the tin oxide coating preferably has the same composition and thickness as that of the coating disclosed in that earlier specification.

The tin oxide coating preferably has a thickness in the range 100 nm to 1200 nm and if thinner than 800 nm is preferably used in conjunction with a colour-suppressing underlayer, for example as described in GB-B-2031756. The tin oxide coating is preferably fluorine-doped.

During the fire testing of the 5 ply laminates described above in which the the outer glass plies consist of float glass, the inventors have found that it is inevitable that the glass pane closest to the fire in the test will delaminate as a result of the bond between the glass and the epoxy resin being broken adhesively. This weakens the laminate structure and leads to a greater chance of through cracking and failure of the laminate.

In an attempt to solve this problem, the inventors employed as the outer glass plies of a 5 ply laminate glass which has been coated with a fluorine-doped tin oxide coating of the type described above. Float glass carrying such a coating is sold by the applicant Pilkington plc under the trade name Pilkington K Glass. The 5 ply laminate had two outer Pilkington K Glass plies each 4 mm thick, a central glass ply of 2 mm float glass and two epoxy resin interlayers of the type described hereinabove, each resin interlayer being 1 mm thick and laminating the float glass to a respective coated outer glass ply of the laminate. This laminate was subjected to a fire test of the type described above.

The inventors discovered surprisingly that the use of such a low emissivity tin oxide coating on the glass ply facing the fire modifies the mechanism under which the thermosetting resin interlayer which is closest to the fire and which incorporates glass forming additives reacts to the heat supplied by the fire. This gives substantial advantages in the use of a low emissivity coating in combination with thermosetting resin interlayers. The use of a low emissivity coating on the surface of the glass ply facing the fire substantially modifies the rate at which the interlayer close to the fire is heated particularly during an initial critical heating period extending over about the first 15 minutes of the fire test.

Figure 2 shows the relationship between temperature and time during a fire test for various parts of both a laminate in accordance with the invention which incorporates a low emissivity coating on the glass facing the fire and a laminate in which that coating is absent and the glass ply facing the fire is of ordinary float glass. The two test results are superposed over each other for comparison. The temperature of the parts of the laminates and the furnace were measured by thermocouples.

The first results of the test carried out on the laminate incorporating the low emissivity coating show that over the test period of around 35 minutes, the temperature inside the furnace increased quite rapidly to over about 800°C. The temperature inside the furnace for the test on the laminate without the coating increased in a corresponding manner. For the test on the laminate with the coating, the outside face temperature, i.e. the temperature of the outside face of the laminate which is remote from the fire, increased much more slowly to a maximum of about 350°C over the period of the test. For the test with the coating, the temperature of interlayer 1 i.e. that interlayer which is closest to the fire, increased relatively slowly for the first 15 minutes of the test and

then increased more rapidly thereafter up to a maximum value of substantially  $800^{\circ}\text{C}$ . For the test on the laminate without the coating, the temperature of the corresponding interlayer 1 increased much more rapidly, and more erratically, over the first 15 minutes of the test, although the ultimate temperature of the interlayer 1 of the laminate without the coating was less than that in the test with the coating. The temperatures for both the test with the coating and the test without the coating for interlayer 2, i.e. the interlayer which was remote from the fire, showed that the temperature of the interlayer in the test without the coating was greater than that in the test with the coating and that the increase in temperature over about the first 15 minutes of the test was greater for the test using the laminate without the coating.

Figure 3 shows more clearly the relationship between the temperatures inside the furnace and of the interlayers 2 for the two tests over the initial heating period in the test of up to about 15 minutes. It will be seen that the rate of increase in temperature of the interlayer 2 in the test without the coating is greater than that for the test with the coating.

The present inventors believe that the mechanism by which degradation of the interlayers 10 and 12 occurs during the heating is substantially modified by employing a low emissivity coating on the inner glass sheet i.e. that sheet which is nearest to the fire. In the test without the coating, the inner glass sheet normally falls off in the initial 15 minute heating period. This occurs because the adhesive bond between the thermosetting resin, namely the epoxy resin, and the glass is broken under heating to elevated temperatures. When a low emissivity coating is employed on the glass face which is exposed to the fire, because the rate of heating over the initial 15 minute heating period is lower than without the low emissivity



coating, the adhesive is given sufficient time to soften before melting during the heating step so that shortly after breakage of the adhesive bond between the epoxy resin and the glass, the softened adhesive can act as a high temperature adhesive which can adhere to the glass. The adhesive can then begin to char and increase in stiffness, thus holding the glass sheet. On breakage of the adhesive bond, there is formed a small gap between the epoxy resin interlayer and the glass sheet resulting from a de-adhesion volume shrinkage. When the adhesive softens, the softened adhesive can take up the small gap formed earlier on de-adhesion. The provision of a gap thus enables instumescient reactions to occur and in particular organic glass forming additives in the interlayer to move to the surface of the interlayer and thereby form a borate and phosphate hydrophilic and ionic surface on the exposed surface of the interlayer. This can bond by hydrogen and partial co-valent bonding to the glass surface. When the epoxy resin interlayer material chars upon further heating, this can lead to consolidation of the bonding between the epoxy resin and the glass by the formation of glass phosphoborates which can bond to the glass surface. The use of a coated inner glass ply allows a greater level of expansion of the thermosetting resin material to take place in a more controlled manner so that there is a shorter time between delamination of the thermosetting resin interlayer and the glass as a result of adhesive bond breakage and softening of the thermosetting resin interlayer. This ensures that the glass ply which faces the fire is more readily adhered in the laminate during the fire test and does not fall off in an early part of the fire test, which occurs with uncoated laminates.

This in turn leads to more controlled heating of the interlayer which is relatively remote from the fire. That interlayer, when a coated glass ply is used, only partly chars giving good bonding between the central glass ply and

the glass ply which is remote from the fire. When an uncoated glass ply is utilised, the interlayer which is remote from the fire can char and undergoes the same reactions as the interlayer which is nearest to the fire.

As is shown in Figure 2, the Insulation Value of a coated laminate in accordance with this aspect of the invention, the Insulation Value being defined as the time taken for the outermost glass surface to reach  $140^{\circ}\text{C}$  above ambient temperature (the outermost surface of course being remote from the fire) is around 14 minutes. This may be compared with a corresponding Insulating Value of an uncoated laminate of around 7 minutes. Thus the use of a low emissivity coated glass ply in accordance with this aspect of the invention surprisingly doubles the Insulation Value of the laminate by modifying the mechanism under which the interlayers are degraded under the action of heat from the fire.

The present invention has been illustrated with reference to the manufacture of cast-in-place interlayers for translucent laminates. The invention may also be employed in conjunction with free-standing pre-formed interlayers of resin material. The structural glass plies in the illustrated laminates are composed of float glass. However, one or more of the glass plies may be annealed or heat or chemically toughened glass. In addition, plastics plies may be employed which are composed of acrylic or polycarbonate plastics material. The term "translucent" is used herein to describe products and materials which transmit light so that they are suitable for glazing applications, whether providing clear through vision, i.e. being transparent or colourless, or not. Preferred translucent reaction mixtures and translucent reaction products in accordance with the invention have a light transmission, through a 2 mm layer thereof, of at least 10%, more preferably at least 20%.

TABLE 1

Example No.	1+2	3+4	5+6	7+8	9+10	11+12	13+14	15	16+17	18+19	20+21
Bisphenol F epoxy resin	61.1	61.1	61.1	71.1	71.1	71.1	71.1.	71.1	71.1	71.1	71.1
DER 736	10.0	-	-	-	-	-	-	-	-	-	-
DER 732	-	10.0	10.0	-	-	-	-	-	-	-	-
Trimethoxyboroxine	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4
TCEP	7.5	5.1	5.1	15.1	15.1	15.1	15.1	10.1	10.1	5.1	5.1
Amgard V6	7.6	10.0	10.0	-	-	-	-	5.0	5.0	10.0	10.0
Borester 7	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
Silane A-187	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Benzyl alcohol	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Gelling Time (Days)	3	5	7	3	3	5	7	3	7	3	7
Tg - °C	38	46	48	50	51	53	55	55	59	61	63

TABLE 2

Example No.	Laminate		Impact Test Result
	Type	T <sub>g</sub> -°C	
1	5 ply	38	Class B - Passed
2	5 ply	38	Class C - Passed
3	5 ply	46	Class C - Passed
4	5 ply	46	Class B - Passed
5	5 ply	48	Class C - Failed
6	5 ply	48	Class C - Passed
7	5 ply	50	Class B - Passed
8	5 ply	50	Class C - Passed
9	5 ply	51	Class C - Passed
10	5 ply	52	Class C - Passed
11	5 ply	53	Class B - Passed
12	5 ply	53	Class B - Failed
13	5 ply	55	Class B - Passed
14	5 ply	55	Class B - Passed
15	5 ply	55	Class B - Passed
16	5 ply	59	Class C - Passed
17	5 ply	59	Class C - Passed
18	5 ply	61	Class C - Passed
19	5 ply	61	Class C - Passed
20	5 ply	63	Class C - Passed
21	5 ply	63	Class B - Passed

TABLE 3

Comparative Example No.	1+2	3+4	5+6	7+8	9+10	11+12
Bisphenol F epoxy resin	61.1	61.1	61.1	65.1	61.1	61.1
DER 736	5.0	-	-	5.0	-	-
DER 732	5.0	10.0	10.0	-	10.0	10.0
Trimethoxyboroxine	8.4	8.4	8.4	8.4	8.4	8.4
TCEP	8.4	5.1	5.1	7.5	5.1	5.1
Amgard V <sub>6</sub>	5.0	10.0	10.0	7.6	10.0	10.0
Borester 7	-	3.3	3.3	3.3	3.3	3.3
Borester 33	5.0	-	-	-	-	-
Silane A-187	0.8	0.8	0.8	0.8	0.8	0.8
Benzyl alcohol	1.3	1.3	1.3	1.3	1.3	1.3
Gelling Time (Days)	3	5	8	3	5	7
Tg - OC	40	41	42	45	46	48

TABLE 4

Comparative Example No.	Laminate Type	Tg-°C	Impact Test Result
1	3 ply	40	Class C - Passed
2	3 ply	40	Class B - Passed
3	3 ply	41	Class C - Failed
4	3 ply	41	Class C - Passed
5	3 ply	42	Class C - Passed
6	3 ply	42	Class C - Failed
7	3 ply	45	Class C - Failed
8	3 ply	45	Class C - Failed
9	3 ply	46	Class C - Failed
10	3 ply	46	Class C - Failed
11	3 ply	48	Class C - Failed
12	3 ply	48	Class C - Failed

CLAIMS:

1. A translucent laminate having impact resistance, the laminate comprising at least three translucent panes which are bonded together by at least two translucent interlayers formed from a thermosetting plastics resin, each pair of adjacent panes being bonded together by a respective one of the translucent interlayers.
2. A laminate according to claim 1, wherein the thermosetting plastics resin is epoxy resin.
3. A laminate according to claim 1 or claim 2 wherein the plies of the laminate are symmetrically disposed relative to a central plane of the laminate.
4. A laminate according to any foregoing claim wherein the laminate has fire resistance and the interlayers incorporate an organic boron-containing glass forming component therein which is not a curing agent for the resin.
5. A laminate according to any foregoing claim wherein the thermosetting plastics resin has a glass transition temperature  $T_g$  ranging from 29 to 63°C.
6. A laminate according to any foregoing claim which is capable of meeting at least Class C of the impact test under BS 6206.
7. A laminate according to any foregoing claim which is capable of meeting the fire test of BS 476 Parts 20 and 22 for a period of at least 30 minutes.
8. A laminate according to any foregoing claim wherein the laminate is up to about 10 mm thick.
9. A laminate according to claim 8 wherein the laminate is about 8 mm thick.

10. A laminate according to any foregoing claim which comprises three plies of glass and two interlayer plies.

11. A laminate according to claim 10 wherein each glass ply is float glass about 2 mm thick and each interlayer ply is about 1 mm thick.

12. A laminate according to any foregoing claim wherein a low emissivity coating is disposed on at least one outer face of the laminate.

13. A translucent laminate substantially as hereinbefore described with reference to Figure 1.

14. A translucent laminate substantially as hereinbefore described with reference to any one of Examples 1 to 21.

15. A method of producing a translucent laminate having impact resistance, the method comprising the steps of providing at least three translucent panes and forming from a thermosetting plastics resin at least two translucent interlayers between the at least three translucent panes whereby a respective one of the translucent interlayers is disposed between each adjacent pair of translucent panes.

16. A method according to claim 15 wherein the interlayers are cast-in-place between the translucent panes.

17. A method according to claim 15 or claim 16 wherein the interlayers are formed by curing the plastics resin, the curing being carried out in a curing step having a first phase in which the resin is partially cured relatively slowly, optionally at a relatively low temperature, and a second phase in which the curing of the resin is completed relatively rapidly, optionally at a relatively high temperature.



18. A method according to any one of claims 15 to 17 wherein the thermosetting plastics resin is epoxy resin.

19. A method according to any one of claims 15 to 18 wherein the plies of the laminate are symmetrically disposed relative to a central plane of the laminate.

20. A method according to any one of claims 15 to 19 wherein the laminate has fire resistance and the interlayers incorporate an organic boron-containing glass forming component therein which is not a curing agent for the resin.

21. A method according to any one of claims 15 to 20 wherein the thermosetting plastics resin has a glass transition temperature  $T_g$  ranging from 29 to 63°C.

22. A method according to any one of claims 15 to 21 wherein the laminate is up to about 10 mm thick.

23. A method according to claim 22 wherein the laminate is about 8 mm thick.

24. A method according to any one of claims 15 to 23 which comprises three plies of glass and two interlayer plies.

25. A method according to claim 24 wherein each glass ply is float glass about 2 mm thick.

26. A method according to any one of claims 15 to 25 wherein a low emissivity coating is disposed on at least one outer face of the laminate.

27. A method of producing a translucent laminate substantially as hereinbefore described with reference to Figure 1.

28. A method of producing a translucent laminate substantially as hereinbefore described with reference to any one of Examples 1 to 21.

29. A method of improving the impact resistance of on impact resistant translucent laminate comprising a plurality of translucent panes and at least one interlayer ply, the or each interlayer ply being formed from thermosetting plastics resin and disposed between an adjacent pair of translucent panes, the total thickness of each of the laminate, the translucent panes and the at least one interlayer ply being predetermined, the method comprising increasing the number of translucent panes and the number of interlayer plies whilst substantially maintaining each of the said predetermined total thicknesses.

30. A method according to claim 29 wherein the thermosetting plastics resin is epoxy resin.

31. A method according to to claim 29 or claim 30 wherein the plies of laminate are symmetrically disposed relative to a central plane of the laminate.

32. A method according to any one of claims 29 to 31 wherein the laminate has fire resistance and the interlayers incorporate an organic boron-containing glass forming component therein which is not a curing agent for the resin.

33. A method according to any one of claims 29 to 32 wherein the thermosetting plastics resin has a glass transition temperature  $T_g$  ranging from 29 to 63°C.

34. A method according to any one of claims 29 to 33 wherein the laminate is about 8 mm thick.

35. A method of improving the impact resistance of a translucent laminate substantially as hereinbefore described with reference to Figure 1.

36. A method of improving the impact resistance of a translucent laminate substantially as hereinbefore described with reference to any one of Examples 1 to 21.

37. A laminate whenever improved by the method of any one of claims 29 to 36 which is capable of meeting at least Class C of the impact test under BS 6206.

38. A laminate according to claim 37 which is also capable of meeting the fire test of BS 476 Parts 20 and 22 for a period of at least 30 minutes.

39. Use as an impact resistant glazing pane of a laminate having a plurality of glass plies with at least one thermoset interlayer between adjacent glass plies, characterised in that to improve the impact resistance the total thickness of glass is divided between at least three separate glass plies and the total thickness of thermosetting interlayer is divided between at least two separate interlayer plies.

**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**section 17 (The Search Report)**

Application number

GB9217327.7

**Relevant Technical fields**

(i) UK Cl (Edition 1) B5N  
(ii) Int Cl (Edition 5) B32B

**Search Examiner**

R J MIRAMS

**Date of Search**

20 MAY 1993

**Databases (see over)**

(i) UK Patent Office

(ii)

Documents considered relevant following a search in respect of claims 1-39

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
E X	GB 2255560 A (PILKINGTON) e.g. Figure 4	at least 1-4,7-11 15,16,18- 20,22-25, 29-32,34 38,39
A	GB 2105652 A (LIN CHII - HSIUNG) Whole document	at least 1-3,8,10, 15,18,19, 22,24,29, 30,31,39
X	GB 2058076 A (GOODYEAR) e.g. Figure 1	at least 1-3,10,15 16,18,19, 24,29,30, 31,39
X	US 3867222 A (PLANT) e.g. Figure 3	at least 1,3,15,19 29,31,39

SF2(p)

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Category	Identity of document and relevant passages	Relevant to claim(s)

#### Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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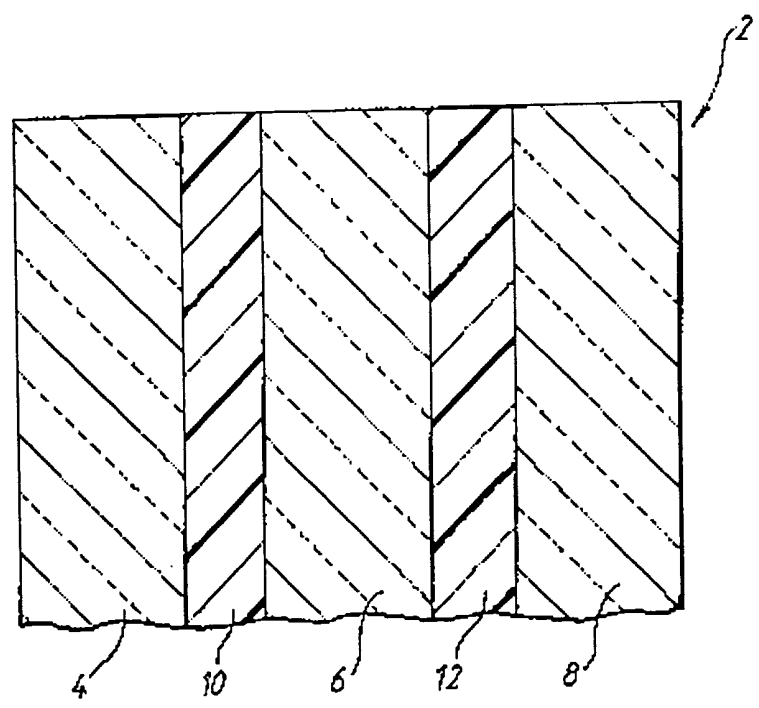


Fig.1

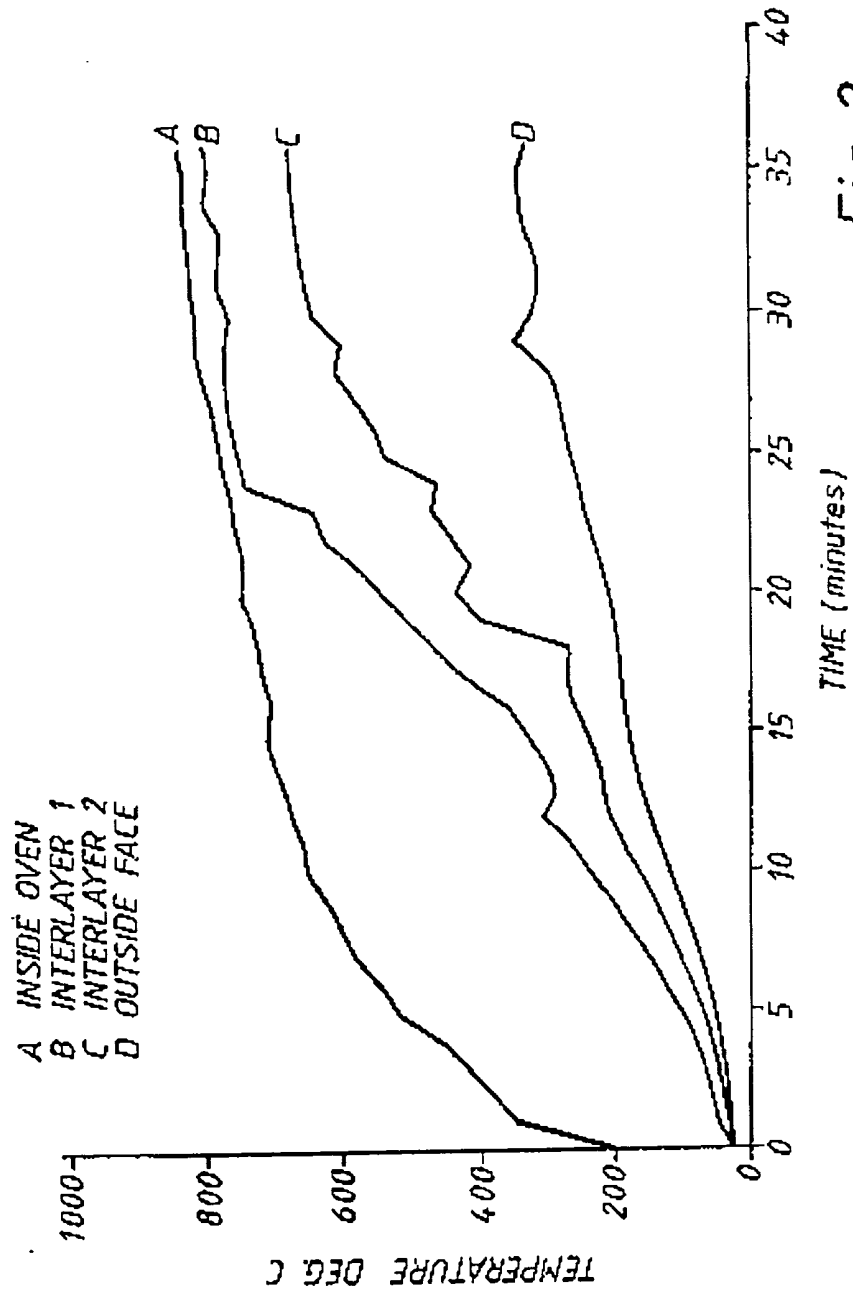


Fig. 2

WITH COATING A — INSIDE FURNACE  
WITHOUT COATING B — INSIDE FURNACE  
C — INTERLAYER 2  
D — INTERLAYER 2

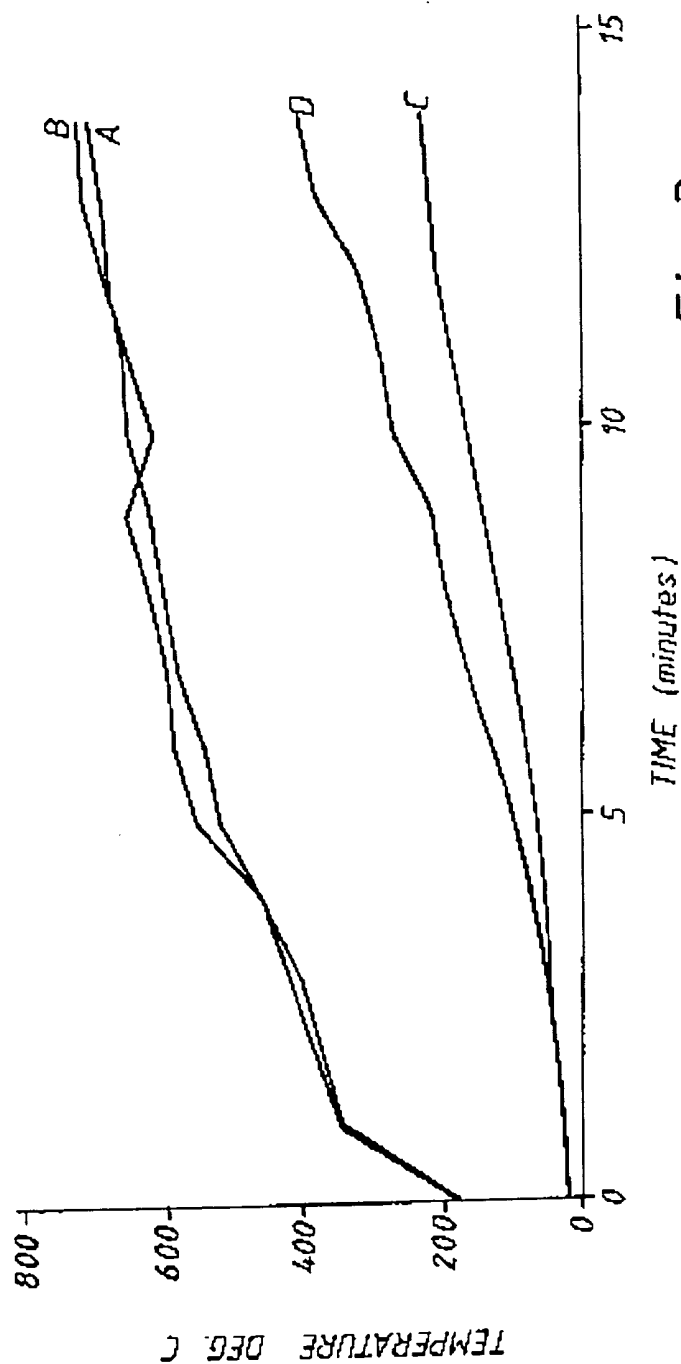


Fig. 3.